THE GRAVIMETRIC DETERMINATION OF MERCURY AND ITS SEPARATION FROM ARSENIC ANTIMONY AND COPPER.

By

CHARLES JOSEPH PRETZFELD, A.B., A.M.

Dissertation

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

NEW YORK CITY

1902

THE GRAVIMETRIC DETERMINATION OF MERCURY

AND ITS SEPARATION FROM

ARSENIC ANTIMONY AND COPPER.

By

CHARLES JOSEPH PRETZFELD, A.B., A.M.

Dissertation

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in the Faculty of Pure Science of

Columbia University.

ACAD. LIBRARY

New York City

1902

Digitized by the Internet Archive
in 2026

PRESS OF
GEO. G. PECK
117 CHAMBERS ST.
NEW YORK

https://archive.org/details/IA41555023_0036

INTRODUCTION.

With the exception of some of the electrolytic methods, no gravimetric method has ever been published by which an accurate estimation of mercury can be obtained. The first purpose of the work described in this thesis was therefore, to find a method which would yield results whose accuracy would be limited by experimental error only, a comparison of the best known methods having been made first. Again, of all the different methods for the separation of mercury from antimony and copper, scattered through the literature of chemistry, no one exists which has not some objection, such as inaccuracy, unnecessary inconvenience, or another fault equally serious. To accomplish this separation in a manner free from objection was the purpose of the second part of this work. Such a separation having been devised, it was proposed to conclusively prove its accuracy by applying it to mercurial tetrahedrite, this mineral being the only one of importance to contain the elements desired.

Unfortunately, the mineral in question was found to be surprisingly scarce. One specimen only, could be procured, notwithstanding serious and repeated efforts, and this contained an amount of mercury so small, that the results, although promising, could hardly be regarded as conclusive evidence of the superiority of one method above the other. In lieu of the natural mineral therefore, an amount of cinnabar, sufficient to yield a reasonably high percentage of mercury, was intimately mixed with a portion of tetrahedrite, and on this mixture analyses were made for comparison.

Some of the known distillation methods were also tried on cinnabar, to find which would give the best results. The electrolytic method was used as standard for comparison. In the following pages, a brief historical outline of the existing methods precedes, in part one, part two and part three, the description of the experimental work.

C. J. P.

QUANTITATIVE CHEMICAL LABORATORY,
HAVEMEYER HALL, COLUMBIA UNIVERSITY,
May 1, 1902.

ACKNOWLEDGMENT.

This work was carried out under the guidance of Professor Edmund H. Miller.

It is with great pleasure that I take this opportunity to express my thankfulness for his sincere interest and for his many suggestions. I wish also, to express my gratefulness for his kindness and encouragement throughout the work.

C. J. P.

QUANTITATIVE CHEMICAL LABORATORY,
HAVEMEYER HALL, COLUMBIA UNIVERSITY,
May 1, 1902.

TABLE OF CONTENTS.

Introduction..... iii

Acknowledgment..... iv

Historical.

Mercury Weighed as Sulphide..... 1

Mercury Weighed as Chloride..... 2

Mercury Weighed as Oxide..... 3

Mercury Weighed as Metal..... 3

By the Application of Reducing Agents in the Cold..... 3

By the Application of Heat to Volatilize the Mercury..... 4

By Electrolytic Deposition..... 5

Experimental.

Estimation of Mercury as Sulphide by the Method of Polstorff and Bulow. 7

Estimation of Mercury as Chloride, by the Method of Hempel..... 8

Estimation of Mercury as Chloride, by the Method of Vanino and Treubert. 9

Estimation of Mercury as Chloride, by the Method of Vanino and Treubert, modified..... 10

Estimation of Mercury as Chloride, by the Method of Rose..... 11

Estimation of Mercury as Chloride, by the Method of Rose, modified..... 11

Estimation of Mercury as Arsenate..... 12

Electrolytic Estimation of Mercury, by the Method of Smith and Kollock. 13

Electrolytic Estimation of Mercury, by the Method of Smith and Wallace. 13

Historical.

Separation of Mercury from Arsenic, Antimony and Copper..... 14

Experimental.

Separation of Mercury from Arsenic, Antimony and Copper, by Acetanilide..... 16

Separation of Mercury from Arsenic, Antimony and Copper by Hydrogen Sulphide in a Cyanide Solution..... 21

Separation of Mercury from Arsenic, Antimony and Copper, by Tartaric Acid, Potassium Cyanide and Hydrogen Sulphide..... 26

Historical.

Analysis of Cinnabar..... 29

Experimental.
Electrolytic Method of Smith and Wallace 29
Chism's Method 30
Distillation Method 32
Historical.
Analysis of Mercurial Tetrahedrite 32
Experimental 33
Analysis of Tetrahedrite, by the Method of Rose and Wöhler 33
Analysis of Tetrahedrite, by the Method described on p. 26 34
Summary of Results 36
Biographical 38

PART I.

THE GRAVIMETRIC DETERMINATION OF MERCURY.

HISTORICAL.

Mercury Weighed as Sulphide.

That mercury can be determined as sulphide has been known for many years. The various methods for the purification of this precipitate however, were not worked upon until Heinrich Rose in 1860 suggested dissolving the sulphide and reprecipitating same. The most important methods of purification are stated in chronological order.

H. Rose, in 1860,[1] suggested that if the precipitate of mercury sulphide is contaminated with any extraneous matter, it should be put in a dilute solution of caustic potash, through which a current of chlorine is passed. During the operation, the heat is raised slightly. The mercury sulphide is converted to the soluble chloride and can be reprecipitated as sulphide, which after washing, is dried and weighed.

J. Volhard, in 1890,[2] proposed a method based on the solubility of mercury sulphide in caustic alkalies in the presence of alkaline sulphides, from which solution, the mercury is again completely precipitated as sulphide by the addition of ammonia salts.

Polstorff and Bulow, in 1891,[3] published the following method: The sulphide is digested with twenty to twenty-five c.cm. of a mixture of equal parts of potassium hydroxide and of potassium sulphide. When completely dissolved, the solution is diluted to a volume of 250 to 300 c.cm. and heated. Am-

---

[1] Pog. An. d. Phys. u. Ch. cx., p. 140.

[2] J. S. C. I., ix., p. 329.

[3] Chem. Cent. Blatt. [4] iii., pt. 2, p. 227.

monium chloride is added and the mercury sulphide formed is filtered from the solution and digested in the cold, with a mixture of hydrochloric acid and potassium chlorate, till dissolved. The solution is heated on a water bath until colorless, after which it is saturated with hydrogen sulphide, filtered, and the precipitate is washed, dried and weighed.

L. Vignon, in 1893,[1] published an article in which he advised using a check filter, through which is passed fifty c.cm. of water, five c.cm. of hydrochloric acid and ten c.cm. of a clear saturated solution of hydrogen sulphide.

Fr. Faktor,[2] states that hyposulphite of soda can be used to produce this precipitate according to the following equation:

$$Na_2S_2O_3 + HgCl_2 + H_2O = HgS + 2NaCl + H_2SO_4.$$

Mercury weighed as Chloride.

Bonsdorff, in 1834,[3] suggested reducing the mercuric salt by adding a large amount of formic acid to an alkaline solution.

Vohl, in 1855,[4] proposed dissolving the substance in nitric acid and evaporating to dryness on the water-bath, after adding an excess of sulphuric acid. All the chlorides excepting those of mercury and silver will be converted to sulphate. The residue is then dissolved in water, and to the solution sodium acetate is first added, and then an excess of silver nitrate. The silver chloride is weighed and from the result, the amount of mercury can be calculated.

Hempel, in 1859,[5] proposed reducing a chloride solution with ferrous sulphate.

Rose, in 1861,[6] suggested phosphorous acid as a reducing agent.

Hager, in 1878,[7] recommended a solution of glucose as a reducing agent.

---

[1] C. N. lxvii., p. 158.
[2] Pharm. Post, xxxiii., pp. 253-254.
[3] An. der Ch. u. Phys. xxxiii, p. 78.
[4] An. d. Ch. u. Pharm. xciv., p. 220.
[5] An. d. Ch. u. Pharm. cx., p. 176.
[6] J. B. xiii., p. 665.
[7] Zeit. fur Anal. Chem. xvii., p. 380.

Thompson, in 1897,[1] suggested the use of a solution of potassium hypophosphite.

Vanino and Trenbert, in 1897,[2] advised that a mixture of peroxide of hydrogen and hypophosphorous acid be used, the peroxide of hydrogen being present to prevent reduction of the subchloride to the metal.

Jannasch and Durselen,[3] proposed the use of hydrazine sulphate.

Mercury Weighed as Oxide.

Marignac, in 1849,[4] proposed heating mercuric salts with nitrogen acids and catching the distillate under water.

Mercury Weighed as Metal.

Under this heading, the history of mercury can be subdivided into three classes:

A. By application of reducing agents in the cold.
B. By application of heat to volatilize the mercury.
C. By electrolytic deposition.

A. By the Application of Reducing Agents in the Cold.

Mitscherlich, in 1827,[5] proposed the use of stanuous chloride as a reducing agent.

Sieveking, in 1875,[6] reduced the sulphide of mercury with cuprous chloride. In this reaction half of the copper will combine with the sulphur and the other half will form a cupric chloride, the mercury being reduced to metallic form according to the equation:

$$HgS. + Cu_2Cl_2 = Hg + CuS + CuCl_2.$$

[1] J. S. C. I. xvi., p. 263.
[2] Ber. xxx., pp. 2808-2809 and Ber. xxxi., 1898, p. 129.
[3] Doctor's Dissertation at Heidelberg, 1899.
[4] J. B. von Liebig u. Kopp, p. 594.
[5] Pog. An. d. Phys. u. Ch. ix., p. 391.
[6] Am. Chemist, vi., p. 160.

Jannasch and Alffers, in 1898,[1] used hydroxylamine chlorhydrate.

Jannasch and Durselen, in 1899,[2] used hydrazine hydrate.

Bennet, in 1900,[3] advised the use of a solution of hypophosphorous acid, with the application of low heat.

B. By Application of Heat to Volatilize the Mercury.

Millon, in 1846,[4] distilled the mercury in a combustion tube, using calcined lime as a desulphurising agent. The distillation was carried on in an atmosphere of hydrogen. In the analysis of mercuric nitrate, copper was used instead of lime.

H. Rose, in 1861,[5] also used a combustion tube, in which he used bicarbonate of soda and calcined lime.

Eschka, in 1872,[6] mixed the compound with iron filings, exposed the mixture to a high heat and the volatilized mercury was caught on a weighed gold plate with which it formed an amalgam.

Attwood, in 1879,[7] used a blow pipe on a mixture, of the mercury compound with a reducing or desulphurising agent, and caught the mercury in a small porcelain crucible containing water.

Schuyten, in 1896,[8] described a method in which he used peroxide of sodium to reduce the compound. The mercury was condensed and weighed.

Chism, in 1898,[9] modified Eschka's method, by using an alcohol lamp in order to avoid too high a temperature, and also by substituting a thin sheet of silver for the gold plate. Iron filings were used to accomplish the necessary reduction.

---

[1] Ber. xxxi. pt. ii., pp. 2381-2385.
[2] Doctor's Dissertation at Heidelberg.
[3] Pharm. J. [4] xi., pp. 575-576.
[4] Erdmann J., xxxvii., p. 271.
[5] Erdmann J., lxxxiv., p. 36.
[6] J. C. S., p. 25.
[7] C. N. xxxix., p. 111.
[8] J. S. C. I. xv., p. 475.
[9] Trans. Am. I. M. E., xxviii., p. 448.

Janda, in 1899,[1] published a method similar to Eschka's gold plate method. As a flux he used manganese dioxide, sodium carbonate, zinc oxide and iron scales.

In addition to these methods, the commonly used fire-assay methods are also worthy of attention. Examples of these can be found in Ricketts and Miller's "Notes on Assaying", and in Furman's "Practical Assaying".

C. By Electrolytic Deposition.

Of the various electrolytic methods by which mercury can be determined, those only were noted in detail, which were considered sufficiently important. The electrolytic methods for the separation of mercury from the other metals, were not studied very thoroughly and will consequently not be considered in this paper.

Hannay, in 1874,[2] published a method in which platinum was used for both anode and kathode. A solution of mercuric sulphate containing little less than one-half gram of mercury was electrolysed. The time required was six hours.

Clarke, in 1878,[3] electrolysed a solution of mercury sulphate. A six-cell Bunsen bichromate battery was employed.

Ludwig and Classen, in 1886,[4] deposited mercury from a solution weakly acid with nitric acid, using a current of, from 0.5 c.cm. to 1.0 c.cm. of electrolytic gas per minute. The concentration of acid was 2 c.cm. per 200 c.cm of solution. Time required was from twelve to fifteen hours.

A. Brand, in 1889,[5] deposited mercury from a double pyrophosphate solution. From this solution about one gram of mercury is deposited in five or six hours by a current of two c.cm. of electrolytic gas per minute.

G. Vortman, in 1891,[6] cites the following methods for the

[1] J. S. C. I. xviii., p. 610.
[2] Am. Chem. iv., p. 193.
[3] C. N. xxxviii, p. 273.
[4] J. C. S. i., p. 493.
[5] J. S. C. I. viii., p. 1011.
[6] J. B., p. 2403 and Chem. Cent. Blatt [4] iii., p. 773.

electrolytic determination of mercury. 1st. From a solution containing an excess of ammonium oxalate. 2d. From a solution acid with tartaric acid, to which an excess of ammonia has been added. 3d. From an alkaline double sulphide solution. 4th. From a solution of the double iodide of mercury and potash.

Rüdorff, in 1892,[1] gives the following methods: 1st. To the solution of mercury, add five drops of nitric acid (sp. gr. 1.2) or of dilute sulphuric acid (1:10). Dilute to one hundred c.cm. and electrolyse with from two to six cells over night. 2d. To the solution of mercury add one-half g. tartaric acid and ten c.cm. of ammonia (sp. gr. 0.91). The current used was from two to six cells. 3d. To the solution containing mercury add five c.cm. of nitric acid, ten c.cm. of a saturated solution of sodium pyrophosphate and ten c.cm. of ammonia. 4th. To the solution add an excess of potassium cyanide and electrolyse.

Smith and Moyer, in 1893,[2] give the following conditions for the electrolytic determination of mercury; Volume, 180 c.cm., containing five c.cm. of nitric acid and 0.1132g. of mercury as metal. The strength of current used is six c.cm. of electrolytic gas per minute. The time required under these conditions is from one half to three quarters of an hour.

Smith and Wallace, in 1896,[3] published the following method: To the solution of mercury containing about 0.2 g. of metal, add from twenty to twenty-five c.cm. of a mixture of equal parts of alkaline sulphide and hydroxide. Dilute to about 125 c.cm. and electrolyse at 70°C. with a current $N.D._{100} = 0.12$ amp. The time required for complete precipitation is about three hours.

Smith and Kollock, in 1899,[4] recommended the following conditions for the electrolysis of a solution containing .1439g. of mercury to which has been added 0.5g potassium cyanide: Volume of solution about 100 c.cm. Current $N.D._{100} = 0.07A.$ and a voltage of 3.2. The temperature used was 65°C, and the

[1] Zeit. fur Angew. Chem., p. 5.
[2] Zeit. fur Anorg. Chem. iv., p. 96.
[3] J. Am. C. S. xviii., p. 169.
[4] Doctor's Dissertation at University of Pennsylvania.

time required for complete deposition of the mercury was about three and one-half hours.

Perreau, in 1900,[1] took 25 c.cm. of a solution of mercuric chloride, containing 0.1159g. of mercury. To this 30 c.cm. of phosphate solution, (Na_2HPO_4, sp. gr. 1.0358) and 5 c.cm. of phosphoric acid were added. The solution was then diluted to 175 c.cm. and electrolysed with a current $N.D._{100} = 0.04A$ and a voltage of 1.6.

Classen,[2] electrolyses an oxalate solution with a current $N.D._{100} = 1.0A$. and a voltage of 5. The time required is five hours.

The Munich Tecknische Hochschule,[3] suggests electrolysing a solution containing not more than five per cent. of nitric acid, at ordinary temperature with a current of $N.D._{100} = 0.5$ ampere. The time required is two hours.

Experimental.

About eight liters of a solution of mercuric nitrate were made, and used for testing the accuracy of various methods for the determination of mercury. The strength of the solution was found to be, by electrolysis, such that each c.cm. contained 0.01673g. of mercury. (Page 13.)

Estimation of Mercury as Sulphide.

The form in which mercury is most commonly weighed being the sulphide, a few experiments were conducted to find how reliable this method is.

Twenty-five c.cm. of the solution of mercuric nitrate was taken and the mercury precipitated, and purified according to the method of Polstorff and Bulow.[4] The solution was diluted

[1] J. S. C. I. xix., p. 53.

[2] Ausgewählte Methoden der Analytischen Chemie, Ed. 1901, p. 49.

[3] Crooke's Select Methods, p. 253.

[4] Chem. Cent. Blatt, 1891, [4], iii., Pt. 2, p. 227.

to a volume of 250 c.cm. and saturated with hydrogen sulphide at 80°c. The precipitate was allowed to settle and then filtered and washed with water containing hydrogen sulphide and a little acid. The mercury sulphide was then dissolved in a solution made up by mixing a 15% solution of caustic potash with an equal volume of a 15% solution of potassium sulphide. The solution of mercury thus obtained was then heated to about 80°C, and a solution of ammonium chloride was added, after having diluted to 250 c.cm. The precipitate of mercury sulphide thus obtained, was allowed to settle, filtered off, washed with a solution of hydrogen sulphide, then twice with water, once with alcohol, twice with carbon desulphide, and again with alcohol, dried at 100°, and weighed as mercuric sulphide. Balanced filter-papers were used.

Results:

$Hg(NO_3^-)_2$ Solution.	Calc. to Hg.	Wgt. of HgS. found.	Calc. to Hg.
25 c.cm.	.41825g.	.4919g.	.4239g.
19 c.cm.	.31787g.	.3734g.	.3216g.
10 c.cm.	.1673g.	.1665g.	.1693g.

In all three determinations the results are somewhat high, the error being about 1.2% of the amount taken. That this is due alone to the presence of free sulphur in with the precipitate, is almost without doubt, as no other impurity could be present. The precipitate settled well in all cases and was easy to handle, the only objection being that it possessed a tendency to creep, and at times adhered rather firmly to the sides of the beaker.

Estimation of Mercury as Chloride.

The first method tried was that of Hempel,[1] and was carried out as follows:

A known quantity of the standard solution of mercury was diluted to 150 c.cm.; 0.3g. sodium chloride, and 1.8g. ferrous

[1] An. d. Chem. u. Pharm., 1859, cx., p. 176.

sulphate were then added and the solution stirred until the salts added had dissolved. Caustic soda was next added until the solution had become alkaline, and the whole was stirred for a few minutes. Sulphuric acid was then added to acid reaction and the solution again stirred The solution was then allowed to stand over night. The precipitate was filtered off and washed once or twice with cold water, dried at 100°C., and weighed.

Results:

$Hg(NO_3)_2$ taken.	Calc. to Hg.	Wgt, of Hg_2Cl_2,	Calc, to Hg,
A) 25 c.cm.	.41825g.	.4898g.	.4161g.
B) 25 c.cm.	.41825g.	.4896g.	.4159g.
C) 25 c.cm.	.41825g.	.4906g.	.4167g.
D) 25 c.cm.	.41825g.	.4905g.	.4166g.
E) 17 c.cm.	.2844g.	.3355g.	.2849g.
F) 15 c.cm.	.2509g.	.2926g.	.2490g.

The results here are all somewhat low, excepting that of experiment E. This however was carried out under exactly the same conditions as the other determinations, and its superior result is probably due to a very small amount of impurity. The error averages a little less than 0.5%. As the precipitate had in all instances, a greyish pink appearance, it was supposed that the error was due to excessive reduction of a very small portion of the mercury taken. It was found perfectly safe to wash the precipitate with a dilute solution of hydrochloric acid (1:10).

The next method tried was that of Vanino and Treubert,[1] in which an excess of sodium chloride is added to the solution of mercury, which should have a volume of about 100 c.cm., and then as a reducing agent a slight excess of a mixture containing one drop of commercial hypophosphorous acid to every cubic centimeter of peroxide of hydrogen, is added drop by drop, while stirring. The solution is allowed to stand one hour, filtered on balanced filters and quickly washed with hydro-

[1] Ber. 1897, xxx., p. 2808–2809.

chloric acid, and finally with water. The temperature used for drying was 105°C.

Results :

Hg. $(NO_3)_2$ taken.	Calc. to Hg.	Wgt. of Hg_2Cl_2	Calc. to Hg.
25 c.cm.	.41825g.	.4893g.	.4156g.
25 c.cm.	.41825g.	.4892g.	.4155g.
21 c.cm.	.35133g.	.4105g.	.3486g.
10 c.cm.	.16730g.	.1955g.	.1660g.
15 c.cm.	.25096g.	.2937g.	.2494g.

The average error by this method was 0.68%, this being in all probability due to the same cause as in the preceding method. The precipitates in these experiments were more nearly white than those obtained by Hempel's method. They were however in a more finely divided condition and at times would run through the paper, even when allowed to settle over night. It was found best to allow the solution to stand about five hours before filtering.

By a very slight modification of this method however, very accurate results were obtained. Instead of converting the mercury to chloride and then reducing, the reducing agent was added first and after stirring for about one minute, an excess of sodium chloride was added. The result was, that a heavy curdy precipitate, very similar in appearance to that of silver chloride, was thrown down immediately and settled very rapidly. The other conditions of the above method were maintained. The accuracy of the results obtained in this manner can be judged from the following table.

Results :

Hg. $(NO_3)_2$ taken.	Calc. to Hg.	Wgt. of Hg_2Cl_2	Calc. to Hg.
13 c.cm.	.21749g.	.2556g.	.2171g.
19 c.cm.	.31787g.	.3736g.	.3173g.
15 c.cm.	.25095g.	.2951g.	.2506g.
15 c.cm.	.25095g.	.2953g.	.2508g.
10 c.cm.	.16730g.	.1972g.	.1675g.
10 c.cm.	.16730g.	.1972g.	.1675g.
10 c.cm.	.16730g.	.1971g.	.1674g.

The explanation for the rapid formation of this precipitate, is that mercury in the form of nitrate is reduced, and this salt of mercury being much more dissociated than the chloride, the reaction takes place in a much shorter period of time. The disadvantage of the above is however, that mercury is usually in the form of chloride, and for this reason, cannot be applied very generally.

The next method tried was that of H. Rose.[1] It was conducted in exactly the same manner as that of Vanino and Treubert, the only difference being that phosphorus acid is used as a reducing agent, and that the precipitate was allowed to settle over night. The results are quite low, probably due to the strong reducing action of phosphorous acid. The precipitate had a greyish color and also showed a tendency to run through the paper. The results obtained are as follows:

Results:

Hg. $(NO_3)_2$ taken.	Calc. to Hg.	Wgt. of Hg_2Cl_2	Calc. to Hg.
25 c.cm.	.4182g.	.4881g.	.4146g.
14 c.cm.	.2342g.	.2726g.	.2316g.
17 c.cm.	.2844g.	.3311g.	.2812g.
13 c.cm.	.2175g.	.2530g.	.2149g.
17 c.cm.	.2844g.	.3313g.	.2814g.
20 c.cm.	.3346g.	.3913g.	.3324g.

Here again, as above, the reducing agent was added before converting the mercury to chloride, with the following success.

Results:

Hg. $(NO_3)_2$ taken.	Calc. to Hg.	Wgt. of Hg_2Cl_2	Calc. to Hg.
10 c.cm.	.1673g.	.1970g.	.1673g.
15 c.cm.	.2509g.	.2959g.	.2514g.
10 c.cm.	.1673g.	.1968g.	.1671g.
10 c.cm.	.1673g.	.1963g.	.1667g.

The quality of the precipitate obtained in this way was the same as that obtained by similarly modifying Vanino and Treubert's method.

[1] J. B. 1861, xiii., p. 665.

Estimation of Mercury as Arsenate.

Since the percentage of mercury in mercury arsenate is smaller than in mercury sulphide or chloride, the error caused by manipulation will of course be smaller than if the mercury formed a larger proportion of the precipitate. That an arsenate of mercury exists, is known,[1] but no attempt had ever been made to weigh the mercury in this form. Those conditions were consequently sought which would precipitate the metal completely and give the most accurate results. By the following method good results were obtained. To a cold solution of mercuric nitrate, of a bulk of about 100 c.cm., about twenty c.cm. of a saturated solution of sodium arsenate was added, this being an excess. A heavy yellowish-white precipitate of mercuric arsenate was immediately formed, and settled rapidly, but in order to ensure complete precipitation, it was found best to allow the solution containing the precipitate to stand for about five hours. The solution was then filtered through balanced papers, and the precipitate was washed with cold water, dried at 95°C. to 100°C. and weighed.

Results :

$Hg.(NO_3)_2$ taken.	Calc. to Hg.	Wgt. of $Hg_3(AsO_4)_2$	Prec. Calc. to Hg.
15 c.cm.	.2509g.	.3674g.	.2509g.
15 c.cm.	.2509g.	.3677g.	.2512g.
15 c.cm.	.2509g.	.3671g.	.2508g.

These results are sufficiently accurate for any requirements, and the method is extremely simple. Unfortunately however, the mercury is not precipitated as arsenate from a chloride solution, thus limiting the application of the method considerably. The presence of a small amount of free nitric acid, did in no way interfere with the accuracy of the results.

Electrolytic Determination of Mercury.

Two methods only were used, the purpose having been more to determine the strength of the standard solution used, than to compare the methods.

[1] Damner's "Anorganische Chemie," ii., p. 921.

In the first method the conditions proposed by E. F. Smith,[1] (page 6), were tried.

Results :

$Hg.(NO_3)_2$	KCN	Dilution	Current	Voltage	Temperature	Mercury found
10 c.cm.	0.8g.	100 c.cm.	$ND_{100}=0.07A$	3.2	65°	.1675g.
10 c.cm.	0.8g.	100 c.cm.	$ND_{100}=0.07A$	3.2	65°	.1673g.

The other method was from a solution of the double sulphide of mercury and potassium. (page 6). The conditions and results were :

$Hg.(NO_3)_2$	K_2S	Dilution	Current	Voltage	Temperature	Mercury found
10 c.cm.	20-25 c.cm.	125-130 c.cm.	$N.D._{100}=0.12A$	2½	70°C	.1672g.
10 c.cm.	20-25 c.cm.	125-130 c.cm.	$N.D._{100}=0.12A$	2½	70°Co	.1673g.

From these results, the strength of the solution in terms of mercury was 0.01673g. for each cubic centimeter.

All of the most important methods for the gravimetric estimation of mercury, having been tried, it was concluded that, when very accurate results are desired, the following methods only, will give satisfactory results.

1st. The method of Vanino and Treubert, as modified, page 10.

2nd. The method of Rose, as modified, on page 11.

3rd The determination of mercury as arsenate, described on page 12.

4th. The determination of mercury by electrolysis.

Unfortunately the first, second and third methods above referred to cannot be used when the mercury is in the form of chloride, the first and second yielding low results, and the third being impossible since no precipitate is formed. The precipitation of mercury as sulphide, on the other hand, permits of very wide application. The precipitation as such is always rapid as well as complete, but if weighed in this form it yields high results on account of the separated sulphur present. The precipitation in this form is however of great value, not only because it acts in many cases as a separation, but also because the precipitate can easily be dissolved and electrolysed from the solution thus obtained, yielding most satisfactory results. This method was used in the succeeding work on the separation of mercury.

1 Doctor's Dissertation of L. G. Kollock at Pennsylvania, 1899.

PART II.

SEPARATION OF MERCURY FROM As., Sb., AND Cu.

Historical.

H. Rose, in 1840,[1] published a method for the separation of mercury from arsenic, antimony, and copper, based on the precipitation of mercury as mercurous chloride, while the other metals remain in solution. In order to insure complete precipitation of the mercury, the solution was allowed to stand for twelve hours. Phosphorous acid was used as a reducing agent.

R. Fresenius,[2] proposed the separation of mercury from antimony, arsenic, and copper, by digestion of the sulphides of these metals with yellow ammonium sulphide, the mercury sulphide being the only sulphide insoluble in this reagent.

Potstorff and Bülow,[3] in 1891, suggested treating the sulphides of these metals with a mixture of equal parts of equally concentrated solutions of caustic potash and potassium sulphide. Arsenic, antimony, and mercury sulphides dissolve, the copper sulphide however, remaining undissolved on the filter. From the solution the mercury is precipitated as sulphide by addition of ammonium chloride, the arsenic and antimony remaining in solution.

v. Uslar,[4] in 1895, published an article on a separation based on the precipitation of mercurous chloride, the reduction being accomplished by phosphorous acid. The precipitate which is

[1] J. B. xiii., p. 665.
[2] Zeit. fur. Anal, Chem. ii., p. 343, 1863.
[3] Zeit fur. Anal. Chem. xxxi., p. 697.
[4] Zeit. fur. Anal. Chem. xxxiv., p. 411.

likely to contain some metallic mercury is dissolved in hydrochloric acid and potassium chlorate, and precipitated as sulphide by saturating with hydrosulphuric acid. The precipitate of mercury sulphide is then dissolved in alkali sulphide and caustic potash, and from this solution is reprecipitated with ammonium chloride and weighed as sulphide.

Jannasch and Lenhert,[1] in 1898, ignited the sulphides in a stream of oxygen and collected the volatilized mercury in nitric acid. To the solution of mercury in the receiver, hydrogen peroxide was added to hasten the solution of mercury. When arsenic is present, the precipitate is mixed with magnesium oxide before ignition.

Jannasch and Devin,[2] proposed the separation of these metals by precipitating mercury as metal from a tartrate solution by a ten per cent. solution of hydroxylamine chlorhydrate.

Jannasch and Durselen,[3] ignite the sulphides in a current of bromine. The volatile mercuric bromide is caught in dilute nitric acid. The mercury is then precipitated by hydrogen sulphide, washed and weighed.

Jannasch and Durselen,[4] separated mercury from an oxalate solution, by precipitating calomel with hydrazine sulphate.

The above methods for the separation of mercury from arsenic, antimony, and copper are based on the precipitation of mercury as calomel, as sulphide, as metal, or by ignition of the mixed sulphides in a current of gas and collection of the volatilized mercury.

The precipitation of mercury as chloride is very slow, requiring in all cases considerable time to ensure complete precipitation, the only exception being the method of Jannasch and Durselen, where only a short time is required. The objection to this method however, is the exceedingly high cost of hydrazine sulphate. Again the precipitate of mercurous chloride always contains a small amount of metal, thus causing low results. If very accurate results are desired, the precipitated

[1] Zeit. fur. Anorg. Chem. xii. [5] pp. 359–364.

[2] Ber. 1898, xxxi., 2. pp. 2377–2385.

[3] Doctor's Dissertation, Heidelberg, 1899.

[4] Doctor's Dissertation, Heidelberg, 1899.

calomel must be dissolved and reprecipitated in some other form.

The ignition of the mixed sulphides on the other hand, is rather inconvenient since it requires a large form of apparatus, and besides this, the metals must be precipitated before the separation can be made, thus requiring an additional precipitation.

The precipitation of mercury as sulphide by ammonium sulphide has also an objection. The results are always somewhat low on account of the slight solubility of mercury sulphide in ammonium sulphide and also in the alkaline sulpho salts of arsenic and antimony.[1]

The separation by hydroxylamine chlorhydrate, in which the mercury is precipitated in metallic form, requires careful manipulation on account of the heaviness of the metal, the smallest loss of mercury causing a considerable deficiency in final results obtained.

The known methods therefore, either affording low results, or requiring an excessive amount of manipulation, a simpler and more accurate method was sought for the separation of mercury from arsenic, antimony and copper.

Experimental.

By qualitative experiment it was found that mercury was not precipitated from an alkaline solution, by an alcoholic solution of acetanilide. Copper and antimony on the other hand, were completely precipitated under these conditions. Tests were made to determine which conditions were best to effect a complete separation of mercury from antimony and copper.

In the following series of experiments, the purpose was to find the broadest conditions possible for the complete precipitation of antimony and of copper, which would not cause a precipitation of mercury.

The caustic potash solution was made by dissolving 75. g. of caustic in one liter of 95% alcohol.

[1] Comey's Dictionary of Solubilites.

The acetanilide solution contained 60 g. of the salt per liter of alcohol.

Solutions of the metals each containing about 1% of metal were also prepared.

Antimony.

In A, the amounts of acetanilide and antimony were kept constant, while the amount of alkali was varied.

	Sb. Soln.	Acetanilide.	KOH.		
A.	10 c.cm.	25 c.cm.	neutral.	Antimony was completely precipitated.	
	10 c.cm.	25 c.cm.	5 c.cm.	excess.	" " " "
	10 c.cm.	25 c.cm.	10 c.cm.	"	" " " "
	10 c.cm.	25 c.cm.	15 c.cm.	"	" " " "
	10 c.cm.	25 c.cm.	20 c.cm.	"	" " " "

In B, the amount of acetanilide was varied, the amounts of metal and alkali having been kept constant.

	Sb. Soln.	KOH in excess.	Acetanilide.		
B.	10 c.cm.	10 c.cm.	5 c.cm.	Antimony was completely precipitated.	
	10 c.cm.	10 c.cm.	15 c.cm.	" " " "	
	10 c.cm.	10 c cm.	25 c.cm.	" " " "	
	10 c.cm.	10 c.cm.	40 c.cm.	" " " "	

From the results of A and B it can be seen that antimony was completely precipitated from neutral solutions and from solutions containing a large excess of alkali. Besides this a large excess of acetanilide had no solvent action upon the precipitate of antimony.

By similar series of experiments conducted with copper and with mercury, the following conclusions were arrived at:

1st. Copper is completely precipitated from a solution of acetanilide which is neutral or alkaline. An excess of alkali has no effect.

2d. The amount of acetanilide may be anything above five c.cm. without exerting a solvent action on the copper precipitate.

3d. To prevent the mercury from precipitating, a large amount of acetanilide is necessary and the solution must be neutral.

4th. The principal function of the organic salt is to hold the mercury in solution.

Those conditions having now been ascertained which promised the best results, quantitative experiments were conducted, to test the accuracy of the separation.

For this purpose, the following solutions were prepared:

A strong hydrochloric acid solution of antimony, containing 1% of metal.

A solution of copper sulphate containing 2% of metal.

An alcoholic solution of caustic potash and an alcoholic solution of acetanilide, both of which were similar in strength to those used for the qualitative experiments.

The mercury solution contained 0.01673 g. mercury per c.cm.

Separation of Mercury from Antimony and Copper.

The separation was tried as follows: To 10 c.cm. of the mercury solution, about 8 c.cm. of the antimony solution ,and 10 c.cm. of the copper solution were added. Part of the antimony was thrown down as a basic salt, due to partial neutralization, caused by addition of the weakly acid solutions of mercury and copper. One hundred c.cms. of acetanilide was now added and the solution was stirred thoroughly. A few drops of corallin were now added, and the solution was then made very slightly alkaline by the alcoholic potash, which was added from a burette. A drop of dilute hydrochloric acid (1:5) was next added to render the solution faintly acid.

The heavy precipitate of copper and antimony formed was allowed to settle for about fifteen minutes, and then filtered from the solution containing mercury. For the filtration, a filter plate, about twelve centimeteres in diameter was used in order to hasten the operation. The precipitate was then washed four or five times with 95% alcohol. The combined filtrate and washings were then saturated with hydrogen sulphide at a temperature of from 50° to 60°C, and the black precipitate of mercury sulphide filtered. As this precipitate was contaminated with a rather large amount of organic matter, it was purified by dissolving in potassium sulphide and potassium hydroxide, and

after having again been heated to about 60°C, the mercury was reprecipitated as sulphide upon addition of ammonium chloride. The precipitate was then filtered from the solution, and washed first with water, then with alcohol, carbon disulphide, and finally again with alcohol. It was then dried at 100°C, and weighed.

Results:

Mercury taken.	Mercury found.
.1673g.	.1953g.
.1673g.	.1727g.
.1673g.	.1787g.

The high results were in all probability due to the presence of small white crystals, mixed in with the precipitate of mercury sulphide. The crystals were visible only after the precipitate was dried. These crystals, probably of organic composition, were found to be very easily soluble in ammonium chloride and in ammonia. The precipitate was free from antimony and copper.

The above experiment was next repeated, with the following modification: Instead of dissolving the mercury sulphide formed, and reprecipitating it as such for purification, the first precipitate of mercury sulphide was filtered on balanced papers and washed, first with alcohol, then with ammonium chloride, and then with water till the washings gave no test for chlorides with silver nitrate. The washing was then continued with alcohol, carbon disulphide and finally again with alcohol. The mercury sulphide was then dried at 100° C. in an air bath, and weighed.

Results:

Mercury taken.	Mercury found.
A .1673g.	.1604g.
B .1673g.	.1609g.
C .1673g.	.1688g.
D .1673g.	.1683g.

Results A and B are low, while C and D are high. The error in the latter is probably due to incomplete washing. The only possible cause, as far as could be seen, for the low resutls

obtained in A and B was that some of the mercury might have been mechanically carried off by the alcoholic vapors escaping during the precipitation by hydrogen sulphide at 60°C. The next experiment was therefore carried out under conditions similar to the above, the only difference having been, that the mercury was precipitated as sulphide at ordinary temperature.

Results :

Hg. taken.	Hg. found.
.1673g.	.1638g.
.1673g.	.1648g.

The error still being rather large, the next experiment was carried out in a nitric acid solution, so that if any metallic mercury had been thrown down by reduction, due to the presence of organic salts, this would be prevented by the nitric acid present. Therefore instead of acidifying with hydrochloric acid as in the preceding cases, the filtrate was made strongly acid with nitric acid before the addition of hydrogen sulphide. The results under these conditions were no better than those obtained from a hydrochloric acid solution.

Results :

Hg. taken.	Hg. found.
.1673g.	.1647g.
.1673g.	.1641g.

By testing the filtrate it was found that no mercury had remained unprecipitated, and therefore the only place where the mercury might have been retained, could be in the heavy precipitate of copper and antimony. In order to free this precipitate of any mercury that might be mechanically withheld, two more determinations were made, under the same conditions as above, the only modification having been a reprecipitation of the copper and antimony.

Results :

Hg. taken.	Hg. found.
.1673g.	.1726g.
.1673g.	.1706g.

All of the above results were obtained by weighing mercury as sulphide, and as these appeared to be fair in comparison with the results obtained in Part I by weighing mercury as sulphide, it was decided that in the following experiment the precipitate should be dissolved in alkali sulphide and the solution thus obtained, electrolysed, thus making the results more reliable. The results were however very low. It was therefore concluded that this method for the separation of mercury from antimony and copper was impossible. Several experiments were next made to find if mercury could be separated from copper by this method. The conditions used were in all respects similar to those used in the preceding experiment. The results were unsatisfactory, being about two and one-half per cent. low.

Results :

Hg. taken.	Cu. taken.	Hg. found.
.1673g.	.1g.	.1631g.
.1673g.	.1g.	.1634g.
.1673g.	.1g.	.1616g.
.1673g.	.1g.	.1642g.

As no good results could be obtained by this method, even by a reprecipitation, it was concluded that some other method might be found which would require less manipulation and give better results. The error is in all probability due a mechanical loss, a little mercury being retained by the heavy precipitate of the other metals. To free this precipitate completely from mercury would require at least three or four reprecipitations, this rendering the method useless. It was observed however, that when mercury was precipitated as sulphide from a cold alcoholic solution, it did not tend to creep or to run through the filter, as was the case when precipitated from a cold aqueous solution.

Separation of Mercury from Copper, Arsenic, and Antimony, by the Use of Hydrogen Sulphide in a Cyanide Solution.

Separation of Mercury from Copper.

Although it was already known that mercury could be separated from copper by saturating a cyanide solution of the two

metals with hydrogen sulphide,[1] no attempt has ever been made to separate mercury from antimony and arsenic by a method based on the same or on any similar principle That this has not been tried, is probably due to the fact that on adding cyanide of potash to a solution of antimony, a heavy white flocculent precipitate is thrown down, which probably consists of potassium antimonate. All of the antimony is however not precipitated. Before attempting to separate mercury from copper, antimony and arsenic, it was considered advisable to test the accuracy of the method of Haidlen and Fresenins, for the separation of mercury from copper alone. The method is as follows: To the solution containing the two metals, copper and mercury, potassium cyanide is added until the precipitate of copper formed, has dissolved, and then three times again as much cyanide is added as was required to dissolve the precipitate. The clear solution is now saturated with hydrogen sulphide. The copper remains in solution and mercury is precipitated as sulphide. The precipitate is allowed to settle, and the solution is then filtered, and the sulphide of mercury after having been washed and dried, is weighed.

As the precipitate possessed a tendency to run through the paper, upon being washed with water, a dilute solution of potassium cyanide was used for washing, thus obviating any danger of loss. Again, instead of weighing the mercury as sulphide, the sulphide was dissolved in about twenty c.cm. of a mixture of equal parts of potassium sulphide and potassium hydroxide, and from this solution, the mercury was determined electrolytically by the method of Smith and Wallace (page 6). Otherwise, the method used was as prescribed by Haidlen and Fresenius, as stated above.

Results:

Hg. $(NO_3)_2$ taken	Hg. $(NO_3)_2$ Calc. to Hg.	Cu. taken.	Hg. found.
9 c.cm.	.1505g.	.05g.	.1497g.
10 c.cm.	.1673g.	.05g.	.1666g.
10 c.cm.	.1673g.	.05g.	.1670g.
10 c.cm.	.1673g.	.05g.	.1667g.

The results obtained were quite satisfactory, but in order to test the method more thoroughly, it seemed advisable to take

[1] Haidlen and Fresenius An. d. Ch. u. Pharm. xliii. p. 144. 1842.

different ratios of copper and mercury. Therefore, as in the above separations the amount of copper was smaller than the amount of mercury, solutions were made, some of which contained approximately equal amounts of both metals, and in some the amount of copper exceeded that of mercury. Several of these solutions were analyzed for mercury.

Results:

Hg. $(NO_3)_2$ taken.	Hg. $(NO_3)_2$ Calc. to Hg.	Cu. taken.	Hg. found.
10 c.cm.	.1673g.	.15g.	.1672g.
10 c.cm.	.1673g.	.15g.	.1674g.
10 c.cm.	.1673g.	.30g.	.1671g.
10 c.cm.	.1673g.	.30g.	.1670g.

These results were accepted as conclusive evidence of the accuracy of the separation of mercury from copper, no matter in what ratio they might exist.

Separation of Mercury from Antimony and Copper.

That antimony if present, would be almost completely precipitated by potassium cyanide was known, and it was furthermore expected that any unprecipitated antimony, existing in solution would not be precipitated by hydrogen sulphide, the solution having been made alkaline with potassium cyanide. Qualitative tests were first made by adding to a solution of antimonic acid, an excess of potassium cyanide. A heavy white precipitate of antimony, probably a basic potassium antimonate, was thrown down and did not redissolve upon addition of a large excess of potassium cyanide. The precipitate was therefore filtered, and the solution tested for antimony, to determine whether the antimony had been completely precipitated. A test for antimony was obtained. Part of the solution containing antimony was then saturated with hydrogen sulphide, but the antimony remained in solution.

The separation of mercury from antimony and copper was carried out as follows:

To a solution containing .1673g of mercury, .10g of copper and .05g of antimony, potassium cyanide was added until alka-

line and then five or six grams of cyanide of potassium was added in excess. The solution was stirred continually while adding the cyanide, and the stirring was continued until all the cyanide was dissolved. A heavy white precipitate of antimony was thrown down and in addition to this a small amount of antimony was thrown down as a black precipitate. This latter precipitate could be seen best on the filter. The black precipitate which was very small in quantity gave a test for antimony, but not for mercury or copper. Another peculiar phenomenon which occurred on addition of an excess of cyanide, was that very small, sharply cut crystals formed, and adhered to the sides of the beaker. These probably consisted of some salt of antimony, as they did not form when copper and mercury alone, were similarly treated. That they are not due to the formation of a cyanate was proven, by adding potassium cyanate to solutions of mercury, copper, antimony, mercury and copper, mercury and antimony, antimony and copper, and of mercury, copper and antimony.

After the precipitates, which consisted of two or three antimony compounds had settled, the solution was filtered. The filtrate was saturated with hydrogen sulphide and the mercury sulphide filtered off. This was washed with a dilute solution of potassium cyanide, and then dissolved as previously, in a mixture of equal parts of potassium cyanide and potassium hydroxide, and the solution thus obtained was electrolyzed.

Results:

$Hg.(NO_3)_2$ taken.	Calc. to Hg.	Cu. taken.	Sb. taken.	Hg. found.
10 c.c.	.1673g.	.10g.	.05g.	.1670g.
10 c.c.	.1673g.	.10g.	.05g.	.1669g.
10 c.c.	.1673g.	.10g.	.05g.	.1664g.
10 c.c.	.1673g.	.10g.	.10g.	.1674g.
10 c.c.	.1673g.	.10g.	.10g.	.1668g.
10 c.c.	.1673g.	.10g.	.10g.	.1668g.
10 c.c.	.1673g.	.20g.	.20g.	.1672g.
10 c.c.	.1673g.	.20g.	.20g.	.1669g.
10 c.c.	.1673g.	.20g.	.20g.	.1668g.
10 c.c.	.1673g.	.30g.	.30g.	.1674g.
10 c.c.	.1673g.	.30g.	.30g.	.1668g.

These results were accepted as proof of the accuracy of the separation of mercury from antimony and copper in all proportions. In order to determine the amounts of antimony and copper present, it would be necessary to dissolve the precipitate of antimony formed by the addition of potassium cyanide, in strong hydrochloric acid, and combine the solution with the main filtrate containing copper and a small amount of antimony. The combined solutions now acid, could be boiled in order to expel the hydrocyanic acid liberated and the antimony and copper separated by any of the well known methods.

It might be interesting to call attention to the fact, that on adding potassium cyanide to a solution of mercury and copper, the solution, although it usually remained colorless, would at times become faintly pink. On addition of this same reagent to a solution of copper, antimony and mercury, a deep blood-red color was always obtained. Although it was not deemed necessary to know just to what this coloration was due, nor to find the composition of the coloring matter formed, nevertheless several qualitative experiments were undertaken to get at the cause, and if possible to prevent this coloration, which rendered it difficult to determine if the solution was clear after filtering. The experiments made were as follows:

To the following solutions an excess of potassium cyanide was added with the results as stated.

Solutions of:

1st. $Hg(NO_3)_2$, remained colorless.

2d. $CuCl_2$, slightly red to pink.

3d. $Hg(NO_3)_2$ and $CuCl_2$, slightly red to pink.

4th. H_3SbO_4, deeper red than that caused by copper.

5th. H_3SbO_4 and $Hg(NO_3)_2$, same as for antimony alone.

6th. Antimonic acid and $CuCl_2$, deep blood red.

7th. H_3SbO_4, $CuCl_2$ and $Hg(NO_3)_2$, same as 6th.

The blood red color seems therefore to be due to the presence of antimony and copper, and is not at all influenced by mercury. Thinking that this coloration might be due to the presence of a cyanate, a series of experiments, analagous to the above was carried out by using potassium cyanate instead of cyanide. The results were however all negative.

Separation of Mercury from Antimony, Arsenic and Copper by the Use of Tartaric Acid, Potassium Cyanide and Sulphuretted Hydrogen.

Separation of Mercury from Antimony and Copper.

In the separation of mercury from antimony and copper by potassium cyanide and hydrogen sulphide, mentioned above, it was somewhat inconvenient to have the antimony precipitate incompletely only, and, in order to avoid this first filtration, a method was sought by which the antimony might be kept entirely in solution. To attain this end, tartaric acid was used. The method finally adopted was as follows:

To a clear solution of the three metals, about thirty cubic centimeters of a saturated solution of tartaric acid was added and the solution stirred for one or two minutes. Potassium cyanide was then added in small amounts at a time, until the solution became clear. While adding latter reagent, it was found necessary to stir the solution continually in order to dissolve the potassium cyanide. Hydrogen sulphide was then led into the solution, until saturated, and the precipitate of mercury sulphide was allowed to settle. This precipitation was performed in the cold, as there is some danger of losing a little mercury with the escaping fumes. The precipitate of mercury sulphide was then filtered, dissolved and electrolysed.

Results:

$Hg(NO_3)_2$ taken.	Calc. to Hg.	Sb. taken.	Cu. taken.	Hg. found.
10 c.c.	.1673g.	.10g.	.10g.	.1672g.
10 c.c.	.1673g.	.10g.	.10g.	.1665g.
8 c.c.	.1338g.	.20g.	.20g.	.1328g.
9 c.c.	.1505g.	.20g.	.20g.	.1509g.
11 c.c.	.1840g.	.30g.	.30g.	.1840g.
12 c.c.	.2007g.	.30g.	.30g.	.2005g.
9 c.c.	.1505g.	.10g.	.30g.	.1510g.
10 c.c.	.1673g.	.10g.	.30g.	.1669g.
8 c.c.	.1338g.	.30g.	.10g.	.1339g.
11 c.c.	.1840g.	.30g.	.10g.	.1844g.

The conditions for this separation were found to be very broad, thus rendering the method one which can be carried out with great facility. The minimum amount of potassium cyanide required, is an excess of one or two grams. It is safer to add an excess of two or three grams so that the solution shall be strongly alkaline. Any excess beyond this amount does no harm. The dilution also permits of wide limits. The smallest bulk which was used in the above determinations was about 150 c.c. and the largest about 500 c.c. In both of these experiments the results were accurate. Furthermore, the solution, alkaline with potassium cyanide was allowed to stand for more than two hours, with no perceptible change. Nor did standing for two or three hours after precipitation with hydrogen sulphide interfere in any way with the final result. The advantage of the tartaric acid in the solution, over the method first attempted, where no tartaric acid was used, is firstly, that no precipitate of antimony is formed, thereby avoiding the necessity of an additional filtration and in case a determination of antimony is required, the dissolution of this precipitate is avoided. The red color formed in the former method is completely absent in the presence of this acid. In most, if not all cases however, the solution becomes pale orange, which is not in the least an objection. Again when no tartaric acid is used, it is always fatal to use potassium cyanide, containing sulphur[1] since mercury is precipitated as sulphide and is consequently filtered off with the antimony and copper. When on the other hand, tartaric acid is present, a black precipitate of mercury sulphide is formed which can be filtered off with the main precipitate of mercury sulphide, precipitated by hydrogen sulphide.

Separation of Mercury from Arsenic, Antimony and Copper.

The next separation attempted under these same conditions was the separation of mercury from arsenic. A solution of sodium arsenate was made up of a strength of about 1 per cent. of metal. The results of the separations were very satisfactory.

[1] Potassium cyanide free from sulphur is a very expensive reagent.

Results:

$Hg(NO_3)_2$ taken.	Calc. to Hg.	As taken.	Hg. found.
8 c.c.	.1338g.	.05g.	.1342g.
10 c.c.	.1673g.	.05g.	.1670g.
11 c.c.	.1840g.	.30g.	.1833g.
9 c.c.	.1506g.	.30g.	.1511g.

To determine if mercury could be separated from antimony, arsenic and copper, experiments were made with the following results:

$Hg(NO_3)_2$ taken.	Calc. to Hg.	Cu. taken.	Sb. taken.	As. taken.	Hg. found.
9 c.c.	.1506g.	.05g.	.05g.	.05g.	.1509g.
9 c.c.	.1506g.	.05g.	.05g.	.05g.	.1507g.

It was also attempted to separate mercury from tin, the results however were very low. This, although it could not be accounted for is of interest since, in the method of Polstorff and Bulow, where mercury is separated by dissolving the sulphide in alkaline sulphide and then reprecipitating it as sulphide on addition of ammonium chloride, some mercury is also withheld by tin if present.[1] The method of v. Uslar,[2] in which phosphorous acid is used to separate mercury from the metals of the fifth and sixth group is useless also, if tin is present. Bismuth and lead, if present, are completely precipitated with the mercury as sulphides, from which they are separated by digestion with alkaline sulphide.

---

[1] Classen "Ausgewählte Methoden der Analytischen Chemie," p. 63.

[2] Zeit. fur. Analyt. Chem, xxxiv. p. 391, 1895.

PART III.

MERCURIAL ORES.

A.—Analysis of Cinnabar.

Cinnabar, being the most important ore of mercury, it seemed well worth while to compare one or two of the most important methods for the determination of that metal therein.

The most important methods for the determination of mercury in cinnabar are:

Classen's method,[1] which is based on the electrolytic precipitation of mercury from a hydrochloric acid solution or a sodium chloride solution in which the mineral is suspended.

Rising and Lenher,[2] decompose the ore in hydrobromic acid, neutralise the solution with caustic potash, add cyanide of potash in excess, and electrolyse with a weak current.

Smith and Wallace,[3] decompose the ore with 20-25 c.cm. sodium sulphide, dilute the solution to 125 c.cm. and electrolyse.

Chism's modification[4] of Eschka's method[5] in which the ore is mixed with a reducing agent. The mixture is heated and the mercury caught on a silver plate.

In addition to these methods, there are distillation methods of importance, all of which have been mentioned on pages 4 and 5.

The electrolytic method of Smith and Wallace[6] was first tried. In this method the cinnabar is decomposed by digestion with alkaline sulphide and caustic alkali and the solution of mercury

---

[1] Ausgewählte Methoden der Analytischen Chemie., Ed. 1901, p. 50.
[2] J. Am. C. S. xviii. p. 96, 1896.
[3] J. Am. C. S. xviii. p. 169, 1896.
[4] Trans. Am. I. M. E. xxviii. p. 148, 1898.
[5] J. C. S. xxv. 1872.
[6] J. Am. C. S. xviii. p. 96, 1896.

thus obtained is diluted to 125 c.cm., and electrolysed at 70°C with a current $ND_{100}=0.12$ amperes.

The results obtained by this method, on a sample of cinnabar were 16.01% Hg. and 16.02% Hg.

Chism's method[1] was also tried with the same sample, but with rather poor success. The description of the method in brief, is as follows: The powdered mineral is mixed with five or six times its weight of iron filings, which have been lixiviated with alcohol and then ignited. The mixture is then covered with about one gram of filings. Heat is then applied with an alcohol lamp for from ten to fifteen minutes, when the flame is removed. After cooling, for from five to ten minutes the silver foil is weighed. The increase in weight is due to mercury. The heating is now repeated for the same length of time, cooled and again weighed The apparatus used is as follows: A retort for which an ordinary annealing cup, such as is used in assaying may be used, a circular tin shield to protect the foil from the heat, a small alcohol lamp with a flame about six centimeters high, which just spreads out over the bottom of the retort or cup, a piece of silver foil about 0.02 m.m. thick used to cover the retort and finally a condenser, for which a platinum dish filled with cold water is placed on the silver foil.

The results obtained by this method were over two per cent. lower than those obtained by the electrolytic method.

Results:

Ore taken.	Weight of Hg. after heating for 15 minutes.	30 minutes.	40 minutes.	Total percentage of Hg. found.
.29755g.	.0404g.	.0007g.	——	13.81%
.22440g.	.0297g.	.0007g.	.0003g.	13.68%

In the above experiments, the silver foil was always allowed to remain undisturbed, after removing the heat for eight minutes, before weighing. These results were very low, and the only explanation for this discrepancy was, that the condenser allowed some of the mercury to escape or that the application of heat was not performed properly. In all of the following

[1] Trans. Am. I. M. E. xxviii. p. 148, 1898.

experiments therefore, instead of using a platinum dish, a copper water-bath was used, the bottom of which had been polished and flattened so as to sit flatly upon the silver foil. To this water bath, a syphon arrangement was attached, and a current of cold water was kept flowing through the bath so that at no time, was there any danger of the condenser becoming warm. Instead of a tin shield, an asbestus disc was used, in order to protect the silver foil as much as possible from the heat. Experiments were now carried on to determine just what heat was necessary to procure accurate results. It was decided to start with a low, and end with a much higher temperature. The ore, after having been mixed with iron filings and placed in the cup, was heated for five minutes with a flame which barely touched the bottom of the cup. It was then allowed to cool for ten minutes, and weighed. The same conditions were repeated twice with the same sample, a freshly ignited piece of silver foil having been used after each weighing. The heat was then raised, by increasing the size of the flame, so that the bottom of the cup was covered by it. Twice the heat was applied for five minutes and the third time this same sized flame was applied for ten minutes. The time allowed for cooling was in all cases ten minutes. The heat was then raised and applied for five minutes at a time until no increase in the weight of the foil could be observed. Finally to make certain that the cup retained no more mercury, a bunsen burner was used. The mercury however had been completely extracted by the alcohol flame.

Results:

Ore taken,	Total mercury found.	Percentage of mercury.	Error.
.1661g.	.0255g.	15.35g.	0.65%
.1301g.	.0197g.	15.14g.	0.86%
.1384g.	.0210g.	15.32g.	0.78%

The results were fairly good, but the time required was about as long as that required in the regular distillation method and the results were no better, although requiring more attention.

In the experiments next tried, the ore was heated for a longer

time with a flame which just covered the bottom of the cup. The time of heating was fifteen minutes, and the time allowed for cooling was twelve minutes. These conditions were repeated only once on the same sample, the purpose of these experiments being to find out if the results would be better by using a moderately high temperature for a fairly long time, thus necessitating fewer weighings.

The amounts of ore taken were: .1384 grams and .4625 grams. The results were: 13.877 Hg., and 13.91% Hg., being in each case over two per cent. low.

Another method tried on cinnabar was the distillation of a large amount of mercury from the ore which had been mixed with iron filings. An ordinary glass retort was used and the mercury was caught in very dilute hydrochloric acid. The purification of the mercury was carried out by treatment with successive portions of dilute hydrochloric acid. It was finally poured into a weighed porcelain crucible and dried after having been washed with alcohol, two or three times.

Results:

Ore taken.	Iron filings taken.	Hg. found.	Percentage of Hg. found.
22.5214g.	175g.	3.5163g.	15.61g.
24 1709g.	180g.	3.7402g.	15.47g.

As the mercury contained in the ore was 16.01%, the results by this method were from four to six-tenths of one per cent. low, this being sufficiently accurate for mercury in most cases, and better than Chism's method, since it required less attention and was just as accurate.

B. Analysis of Mercurial Tetrahedrite.

Most of the methods for the decomposition and analysis of tetrahedrite have already been described under the methods given for the separation of mercury from arsenic, antimony and copper, and for the estimation of mercury by distillation. The decomposition of the mineral is best accomplished by heat-

ing in a stream of oxygen (page 15), or bromine (page 15), or chlorine. Other methods, as those included under the titles: "Mercury weighed as metal" (page 3), and "Mercury weighed as chloride" (page 2), are employed for the separation and determination of mercury after the mineral has been decomposed. The manner in which the mineral is usually decomposed, is by the method of Rose and Wöhler,[1] which is as follows for the determination of mercury.

The apparatus used consists of a chlorine generator, a piece of hard glass tubing about five or six inches long containing a bulb blown at each end, the sample to be analysed being placed in the first bulb. This tube is connected at one end with the drying apparatus and at the other end with one or two U tubes, containing a mixture of equal parts of hydrochloric and tartaric acids. The second U tube is connected with a flask containing cautic potash, which absorbs most of the escaping chlorine. After placing one gram of the mineral in the bulb nearer the chlorine generator, the apparatus is connected and a slow stream of chlorine is allowed to pass over the sample. About five minutes after the current has started, a low heat is applied with a Bunsen burner, to the bulb containing the sample, and continued for about ten minutes after fumes of ferric chloride are seen. The chlorine is allowed to pass over the mixture until latter is cooled, when the hard glass tube is cut between the bulbs, and that part of the apparatus containing the volatile portion of the mineral is sealed with rubber caps or rubber stoppers so that the chlorine does not escape. The volatile portion of the mineral is caught in the second bulb and in the U tubes, which are allowed to stand over night. It is then washed into a beaker with water, and the solution is filtered. The filtrate is then heated to about 60° C. and saturated with hydrogen sulphide. The precipitate formed is digested with ammonium sulphide, and the solution thus formed is filtered from the residual precipitate, which consists of mercury sulphide together with sulphides of lead, zinc and bismnth. To separate the mercury, the precipitate is digested with a mixture of equal

[1] Rose "Analyse Quantitative", p. 295.

parts of sodium sulphide and sodium hydroxide and from the solution thus obtained the mercury is preciptated as sulphide upon adding ammonium chloride, and is either weighed as such or redissolved and electrolysed.

The apparatus used in this work was the same as just described, the only difference being in the hard glass tubing in which the sample is placed. Instead of using a tube with two bulbs, one at each end, a tube was made in the following manner: A piece of tubing such as is used for organic combustions was drawn out at one end into a narrow tube about a foot long and about one-third of an inch in diameter. At that part of the tube where the diameter decreases, a bend of ninety degrees was made. This form of tubing was considered superior to that described above, since it was much more easily made and could be used for several determinations, by cutting off only about an inch above the U tube after each decomposition. Furthermore, instead of putting the powdered sample directly into the tube, the sample was put into a percelain boat and this was put into the stout part of the tube. The entire volatile portion of the mineral can be driven into the U tubes by cautiously applying heat to it, in whatever portion of the tube it may condense. The analysis of the volatile portion of the mineral, was executed in the manner above described. The results obtained by this method were compared to results obtained by applying the method described on page 26, which was carried out as follows:

The mineral was decomposed in the same manner as described above. To the filtrates obtained from the contents of the receivers and washings, from thirty to forty c.cm. of a saturated solution of tartaric acid was added. Sticks of cautic potash were then added until a heavy precipitate of potassium antimonate was formed, and then potossium cyanide was added until the solution became perfectly clear, after which about four grams was added in excess. In neutralizing, care was taken that the temperature did not rise too high, by adding the reagent slowly. Hydrogen sulphide was then lead into the clear solution at ordinary temperature, until saturated. The precipitate of mercury sulphide was allowed to settle, and the solution was filtered. The precipitate was then washed, first with a dilute

solution of potassium cyanide, then with a dilute solution of nitric acid, and finally, dissolved in alkaline sulphide and electrolyzed.

Although earnest and repeated efforts were made to procure specimens of mercurial tetratedrite, the only one that could be obtained contained but 0.3% of mercury. This was considered too low to show a just comparison of the methods, so a mixture of cinnabar and tetratedrite was made and analysed in the same way.

Results:

Amount of mineral taken.	Mercury found.	Percentage of mercury.	
0.9153g.	.0012g.	0.13	Method of Rose and Wöhler.
1.0474g.	.0014g.	0.13	
1.0500g.	.0015g.	0.14	
1.1986g.	.0042g.	0.35	Tartaric acid and potassium cyanide method.
1.0278g.	.0039g.	0.38	
Amount of mixture taken.			
.8581g.	.0756g.	8.81	Method of Rose and Wöhler.
.8989g.	.0805g.	8.95	
1.0310g.	.0931g.	9.03	
.8853	.0845g.	9.54	Tartaric acid and potassium cyanide method.
.9139	.0874g.	9.56	
.8592	.0814g.	9.47	

These results show conclusively that the separation of mercury from arsenic, antimony, and copper, by the use of tartaric acid and potassium cyanide is more complete and consequently more accurate than by the use of ammonium sulphide.

Chism's method also was tried on the tetrahedrite, with good results. This seems to prove this method very good for ores running low in mercury.

The results obtained by Chism's method were 0.27% and 0.33% of mercury.

Summary of Results.

The conclusions drawn from the experimental work of Part I, are as follows:

I. By weighing mercury as sulphide, high results, due to the presence of separated sulphur, are always obtained.

II. Results obtained by weighing mercury as mercurous chloride are always low when mercury is thus precipitated from a chloride solution.

III. Accurate results cannot be obtained by precipitating and weighing mercury as mercurous chloride, from a nitrate solution unless the mercury is reduced before it is converted to chloride, in which case the results are very satisfactory.

IV. By precipitating mercury as arsenate by sodium arsenate, very accurate results can be obtained. This method however, cannot be used when the mercury is in a chloride solution.

V. Electrolytic methods are accurate and admit of most general application.

The conclusions drawn from the experimental work of Part II, are as follows:

I. The separation of mercury from antimony and copper, by the use of acetanilide is only qualitative.

II. Mercury can be completely separated from copper in all proportions by saturating a solution, alkaline by potassium cyanide, with sulphuretted hydrogen.

III. Mercury can be completely separated from antimony and copper in all proportions by saturating a solution, alkaline by potassium cyanide, with sulphuretted hydrogen. If antimony also is to be determined the method is somewhat inconvenient.

IV. Upon addition of potassium cyanide to a solution of antimony and copper, a red coloration is produced, which seems to be due to the presence of antimony and copper, and is independent of mercury.

V. Mercury can be accurately separated from antimony and copper by adding to a solution acid with tartaric acid, cyanide

of potassium until alkaline, and then saturating with sulphuretted hydrogen at ordinary temperature.

VI. When tartaric acid is present no red coloration is formed, and all of the antimony present is completely retained in solution.

VII. Mercury can be separated from arsenic, antimony and copper, in the same manner as described under V.

VIII. Tin when present, renders the method useless.

The conclusions drawn from the experimental work of Part III are as follows:

I. Chism's method for the determination of mercury yields very low results, unless excessive care is devoted to the regulation of temperature.

II. By mixing cinnabar with a large excess of iron filings, distilling the mercury and weighing it as such, approximately accurate results can be obtained.

III. The method of Rose and Wöhler as generally used for the analysis of mercurial tetrahedrite yields low results.

IV. By applying the separation mentioned in VI., Part II., to mercurial tetrahedrite, accurate results can be obtained.

BIOGRAPHICAL.

Charles Joseph Pretzfeld entered the College of the City of New York in June, 1892, and was enrolled as a senior in Columbia College in September, 1897, where he received the degree of A. B. in 1898. Studied under the Faculty of Pure Science of Columbia University for the degree of Ph. D., September, 1898, until June, 1902, receiving the degree of A. M. in 1900.